Cu spin reorientation in $Tl(BaSr)PrCu_2O_7$

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The Cu spins in $TlBa_2PrCu_2O_7$ order at $T_N \approx 370$ K with a spin structure that is collinear and is characterized by the $\{\frac{1}{2}\frac{1}{2}1\}$ wave vector, where the nearest neighbor spins are aligned antiparallel along all three crystallographic directions. If 50% of the Ba atoms are randomly replaced by the smaller Sr atoms to form $Tl(BaSr)PrCu_2O_7$, the T_N of the Cu spins reduces to 350 K but the magnetic structure that forms below T_N is the same. However, at $T \approx 20$ K the Cu spins undergo a change in structure, and the spin arrangement is then characterized by the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ wave vector below $T \approx 12$ K. The ground state spin structure of the Cu ions in $Tl(BaSr)PrCu_2O_7$ is hence noncollinear, where the spin directions of the nearest neighbor Cu ions in the ab plane remain collinear and antiparallel while along the c axis they are orthogonal. These results demonstrate that the atoms in the BaO layers are also actively participating in the coupling between the Cu ions. © *1996 American Institute of Physics.* [S0021-8979(96)02808-9]

There are two copper–oxygen layers per unit cell in $TlBa_2PrCu_2O_7$, and both of them are the so-called ''CuO_2-plane'' layers in which O atoms are present between the Cu atoms along both the a and b axes.[1] Neutron diffraction measurements[2] have shown that the magnetic coupling between the Cu spins is antiferromagnetic in nature, and they order at $T_N \approx 370$ K with a spin structure that is identical to the ''plane ordering'' observed[3] in the 1:2:3 system where the nearest neighbor Cu spins are aligned antiparallel along all three crystallographic directions. The moment direction is in the tetragonal ab plane with a saturated ordered moment $\langle \mu_z \rangle = 0.59\ \mu_B$, and this spin structure of Cu remains unchanged down to $T = 1.36$ K. Specific heat data[4] also show a sizable linear term that is comparable to that found in heavy fermion systems.

To study the role that the atoms in the BaO layers play in the Cu magnetism, neutron diffraction and ac susceptibility measurements have been performed on the $Tl(BaSr)PrCu_2O_7$ compound, where 50% of the Ba atoms in $TlBa_2PrCu_2O_7$ have been replaced by Sr atoms. Structural analysis via high-resolution neutron diffraction has shown that the Ba and Sr atoms in $Tl(BaSr)PrCu_2O_7$ are randomly mixed in such a way that on average there are two $(Ba_{0.5}Sr_{0.5})O$ layers, rather than one BaO and one SrO layer, in a unit cell. The magnetic studies that we are reporting here show that the replacement of Ba atoms by Sr causes only a slight reduction in the ordering temperature of the Cu spins, but increases the saturated ordered moment by 50%, and alters the ground state spin structure of Cu ions.

A polycrystalline sample of $Tl(BaSr)PrCu_2O_7$ was prepared by the solid-state reaction from fine powders, and the details of the preparation procedure can be found elsewhere.[5] Neutron diffraction measurements on the combined powder samples were performed at the Research Reactor at the U.S. National Institute of Standards and Technology. The data were collected using the BT-9 triple-axis spectrometer operated in double-axis mode. A pyrolytic graphite PG(002) crystal was used to extract neutrons of energy 14.8 meV (2.351 Å). A PG filter was also employed to suppress higher order wavelength contaminations, and the angular collimations used were $40'$-$48'$-$48'$. About a 10 g powder sample was mounted in a cylindrical aluminum can, and a pumped ^{4}He cryostat was used to cool the sample.

Neutron diffraction patterns were taken at several different temperatures to study the intensity variations with temperature. Similar to what has been observed[3] in $TlBa_2Cu_3O_7$, the $\{\frac{1}{2}\frac{1}{2}1\}$ magnetic reflection that characterizes the Cu spin ordering is observed below 350 K. However, below $T \approx 20$ K this intensity was found to decrease. Figure 1 shows the difference between the diffraction patterns taken at $T = 15$ K and $T = 50$ K. The solid curve is a fit of the observed Bragg peaks to the Gaussian instrumental resolution function, with the dashed line being the base line, and the indices shown are based on the chemical unit cell. A negative amplitude was obtained for the $\{\frac{1}{2}\frac{1}{2}1\}$ peak, clearly indicating a reduction in the $\{\frac{1}{2}\frac{1}{2}1\}$ intensity as the temperature is reduced from 50 to 15 K, while the intensities of both the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ reflections increase. Hence there is a change in the magnetic structure, with the magnetic unit cell doubling in size along the c axis.

A more complete temperature dependence of the magnetic intensities is shown in Fig. 2, where the peak intensities of the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and the $\{\frac{1}{2}\frac{1}{2}1\}$ reflections measured over a temperature range of 1.4 to 450 K are presented. Clearly, the $\{\frac{1}{2}\frac{1}{2}1\}$ intensity starts to develop at $T_N \approx 350$ K. This intensity increases on cooling in the usual way, and reaches saturation at $T \approx 220$ K. At $T \approx 20$ K, however, the $\{\frac{1}{2}\frac{1}{2}1\}$ intensity starts to decrease, and at low temperatures no significant magnetic intensity remains. This is accompanied by the development of the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ types of peaks, demonstrating that the Cu spins undergo a change in structure.

A half-integer value for the c axis miller's index means that the magnetic unit cell is double the chemical one along that axis direction.[6] We note that in each chemical unit cell

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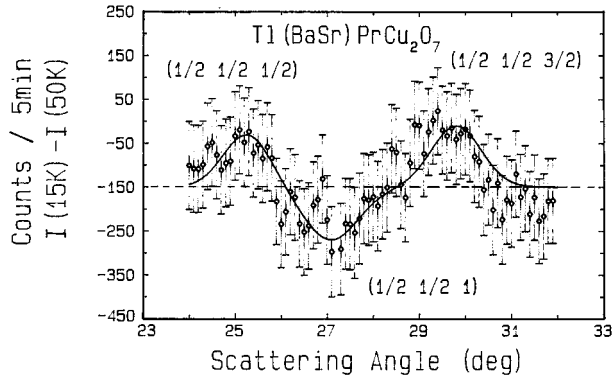

FIG. 1. The difference between the diffraction patterns taken at $T=15$ K and $T=50$ K. As temperature is reduced from 50 to 15 K, the $\{\frac{1}{2}\frac{1}{2}1\}$ intensity decreases while the intensities of the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ reflections increase. The solid line is a fit to the Gaussian instrumental resolution function with the dashed line indicating the base line.

there is one Cu ion along the a and b axes while there are two along the c axis.[1] The magnetic unit cell for the high-T phase, which is characterized by the $\{\frac{1}{2}\frac{1}{2}1\}$ wave vector, hence contains two Cu ions along each crystallographic direction. The proposed Cu spin structure for the high-T phase is a collinear one, where the nearest neighbor spins alternate in direction along all three crystallographic directions, as shown in Fig. 3(a). The moments lie in the ab plane; however, its specific direction with the ab plane cannot be determined from our powder measurements. In Fig. 3(a) we have simply chosen the moment direction of the Cu spins to be along the a axis for clarity. This is the same Cu spin structure as the one observed for $TlBa_2PrCu_2O_7$,[2] $TlBa_2YCu_2O_7$,[7] and $NbBa_2NdCu_2O_8$.[8] Furthermore, by comparing the $\{\frac{1}{2}\frac{1}{2}1\}$ intensity obtained at $T=50$ K to the {001} nuclear intensity, a saturated ordered moment of $\langle\mu_z\rangle=0.89\pm0.05\ \mu_B$ was obtained for the Cu ions. This value of the ordered moment is 50% larger than the 0.59 μ_B obtained for $TlBa_2PrCu_2O_7$.

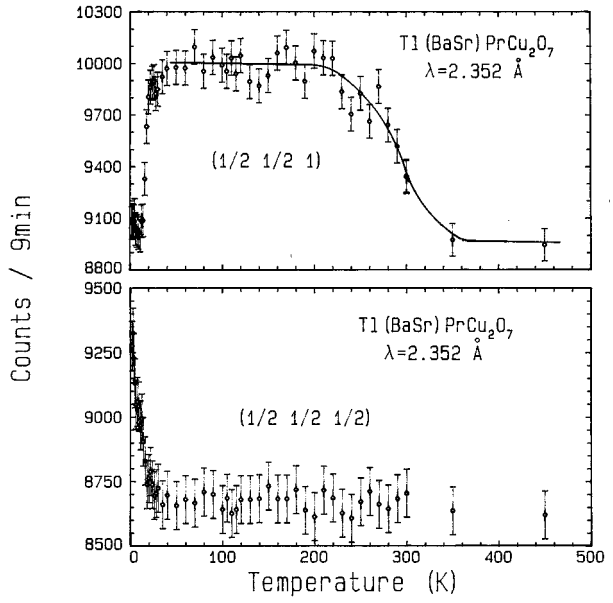

FIG. 2. Temperature dependence of the (a) $\{\frac{1}{2}\frac{1}{2}1\}$ and (b) $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ intensities observed in $Tl(BaSr)PrCu_2O_7$. The ordering temperature of the Cu spins is determined to be $T_N\sim350$ K, and the solid curve is a guide to the eye only. The downturn in the $\{\frac{1}{2}\frac{1}{2}1\}$ intensity at low temperature is accompanied by the development of the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ intensity, and signifies a Cu spin reorientation to a new magnetic structure occurs in this temperature range.

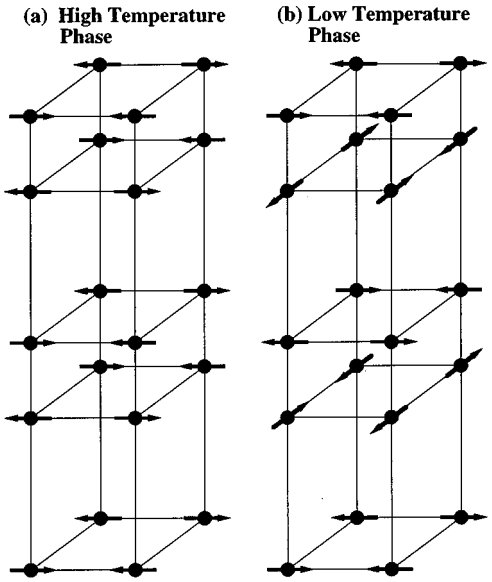

FIG. 3. The Cu spin configurations observed in $Tl(BaSr)PrCu_2O_7$ at (a) high and (b) low temperatures. At high temperatures the nearest neighbor Cu spins alternate along all three crystallographic directions, while at low temperatures the nearest neighbor Cu spins along the c axis are orthogonal.

Below the second magnetic transition at 20 K the magnetic unit cell along the c axis also becomes double the chemical one, which means there are four Cu ions along the c axis in the magnetic unit cell. The simplest Cu spin arrangement along the c axis is the one where the spin directions of the nearest neighbor Cu ions differ by 90°. The nearest neighbor spins along the a and b axes, on the other hand, remain antiparallel. This low-T phase for the Cu spin structure is noncollinear and is shown in Fig. 3(b). The proposed spin structure is supported by the observed relative intensity between the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ and $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ reflections, assuming the magnitude of the moments on the two CuO_2 layers are the same. Moreover, the value obtained for $\langle\mu_z\rangle$ using the $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ intensity observed at $T=1.4$ K is the same value, within experimental accuracy, as the one obtained in the high-T phase. This result further supports the argument that the downturn in the $\{\frac{1}{2}\frac{1}{2}1\}$ intensity together with the development of the $\{\frac{1}{2}\frac{1}{2}\frac{3}{2}\}$ intensity are simply due to Cu spin reorientation.

At intermediate temperatures, i.e., below 20 K and above 12 K, the Cu spin structure may be obtained by superimposing the structures of the high-T and low-T phases, with a weighting which depends on temperature. A noncollinear Cu spin structure such as the one found for the low-T phase is still obtained in this temperature range, but the angle between nearest neighbor Cu spins along the c axis varies continuously with temperature.

The ac susceptibility was measured using a Lake Shore 7221 ac susceptometer. Polycrystalline samples of ~1g were loaded into a cylindrical plastic container which has a height

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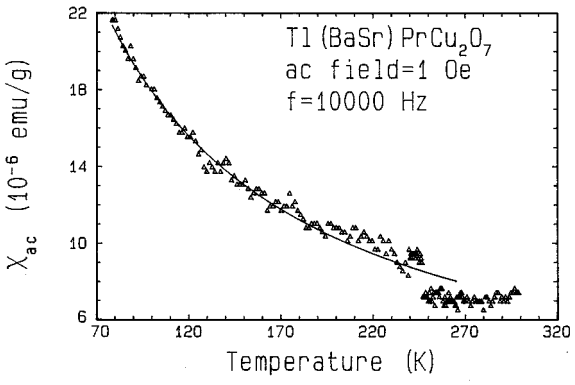

FIG. 4. Portion of the in-phase component of the ac susceptibility measured as a function of temperature. The solid line is a fitted Curie–Weiss curve using the data collected in the temperature range of 30–200 K. The susceptibility shows a sudden drop around 240 K, that signifies the Cu spin disordering.

much greater than its radius, and a conventional ^{4}He flow cryostat was used to cool the sample, with a lowest achievable temperature of 4.5 K. Figure 4 shows a portion of the in-phase component of the *ac* susceptibility measured with a driving magnetic field of 1 Oe and frequency 10^4 Hz. Measurements made using a different field strength or a different frequency generated the same results, indicating the Cu spin relaxation rate is far beyond the frequency used, as expected. The low-temperature portion of the data shown in Fig. 4 may be well described by the Curie–Weiss law, and the solid line shown is a fit of the data to $\chi_0+C/(T+\theta)$ for 30 K$<T<$200 K. This Curie–Weiss behavior signifies the paramagnetic state of the Pr spins, which order at $T\approx 5$ K. Around 240 K, the susceptibility is seen to depart from the Curie–Weiss line shown, which is where significant Cu spin disorder begins to occur.

In summary, we have studied the Cu spin ordering in $Tl(BaSr)PrCu_2O_7$ by neutron diffraction and ac susceptibility measurements. By comparing the results obtained in the present study to that obtained previously[2] in $TlBa_2PrCu_2O_7$, it is clear that the atoms in the BaO layer are also actively participating in the magnetic coupling between the Cu ions, especially along the *c* axis. Although both the Ba and Sr ions have a valence state of 2+, replacing Ba^{2+} by the smaller Sr^{2+} should still lead to a modification of the hybridization among the atoms in the unit cell. The present studies show that the coupling between the Cu spins along the *c* axis is affected more strongly by the substitution than those in the *ab* plane. As 50% of the Ba atoms are replaced by Sr atoms, the T_N of the Cu spins is only slightly reduced, while the ground state spin structure is changed from a collinear spin state into a complicated noncollinear spin state. It would be interesting to see how the Cu spin structure is changed by different degrees of substitution.

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